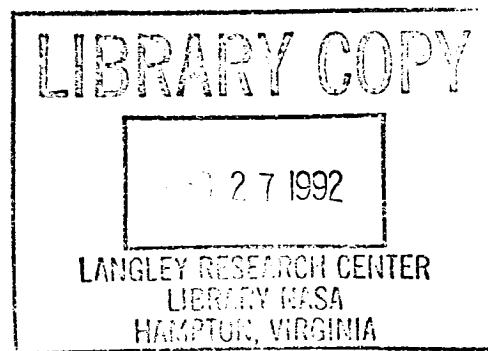


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Trifluoromethyl Groups**

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Introduction

As part of an effort to develop high performance structural resins for aerospace applications, work has continued on block copolymers containing imide and arylene ether segments. The copolymers reported herein represent an extension of previous work¹⁻³ on imide/arylene ether copolymers. The arylene ether block used in this study contains a hexafluoroisopropylidene group in the polymer backbone while the imide block also contains a hexafluoroisopropylidene as well as a pendent trifluoromethyl group in the polymer backbone⁴. The presence of these groups should impart radiation stability as well as solubility in the copolymers. A few copolymers containing an imide block and some other block have been reported. Most notably, the copolymers containing imide and siloxane blocks have received considerable attention⁵⁻⁸ and more recently, polyimide-polyformal block copolymers⁹ and triblock copolymers containing imide-aryl ether phenylquinoxaline blocks¹⁰ have been reported. The preparation of amine-terminated sulfones by a method similiar to that used herein has been reported.¹¹

Experimental

Monomers - 2,2-Bis(4-hydroxyphenyl)hexafluoropropane(6AF) was obtained commercially and recrystallized twice from toluene to yield a white solid, m.p.160-161°C. 4,4'-Difluoro-benzophenone(DFBP), m.p.106-107.5°C, and 3,5-diamino-benzotrifluoride(DABTF), m.p. 86.5-88°C, were used as received from Kennedy and Klim, Inc. and Occidental Chemical Corp., respectively. 2,2-Bis(3,4-dicarboxy-phenyl)hexafluoropropane dianhydride(6FDA) was obtained from Hoechst Celanese Corp. and sublimed at 210-220°C in vacuo to yield a white solid, m.p. 242.5-244°C. 4- aminophenol, m.p. 185-187°C, was purified by sublimation in vacuo at 160-170°C.

Oligomers - The amine-terminated poly(arylene ethers) (ATPAE) were synthesized as shown in Eq. 1 by aromatic nucleophilic substitution of DFBP with 6AF and 4-aminophenol in N,N-dimethylacetamide (DMAc) using potassium carbonate. The oligomers were prepared at two different calculated number average molecular weights (\bar{M}_n) by adjusting the monomer ratio (6AF/DFBP) to 0.85 and 0.92 to provide \bar{M}_n s of 3250 and 6500 g/mole, respectively. The anhydride-terminated polyamide acids were prepared in DMAc as shown in Eq. 2 by adjusting the monomer ratio (DABTF/6FDA) to 0.83 and 0.91 to provide calculated \bar{M}_n s of 3250 and 6500 g/mole, respectively.

Copolymers - The copolymers were prepared by adding a DMAc solution of the ATPAE to the anhydride-terminated polyamide acid solution and stirring overnight under nitrogen. For example, to prepare ATPAE 3250/PI 3250 block copolymer, 6FDA (3.1097g, 7.000 mmol) was added to a solution of DABTF (1.0295 g, 5.845 mmol) and DMAc (24 ml). The mixture was stirred for 6 h to form a clear solution. A solution of ATPAE 3250 (4.1392 g, 1.274 mmol) in DMAc (24 ml) was added to the

polyamide acid solution prepared above to form a clear, viscous solution which was stirred overnight. These block copolymers could be solution imidized by adding toluene to the reaction and heating at 160°C overnight under a nitrogen atmosphere and a Dean-Stark trap. The soluble block copolymer could be cast as a film and dried or precipitated into water to provide a fiberous solid.

Homopolymers- The DATBF/6FDA polyimide (PI) was prepared by addition of a stoichiometric amount of 6FDA to a stirred solution of DABTF in DMAc. The polyamide acid film was thermally imidized in air at 300°C or solution imidized and precipitated to provide a powder for molding. The DFBP/6AF poly(arylene ether) (PAE) was synthesized by the aromatic nucleophilic substitution of a stoichiometric amount of DFBP with 6AF in DMAc/toluene using potassium carbonate as the base.

Characterization - Melting points were determined using a Thomas-Hoover capillary apparatus and are uncorrected. Inherent viscosities (η_{inh}) were obtained on 0.5% solutions in DMAc at 25°C. Differential scanning calorimetry (DSC) was performed at a heating rate of 20°C/min with the apparent T_g taken at the inflection point of the ΔT versus temperature curve. Thermogravimetric analysis (TGA) was conducted on film specimens at a heating rate of 2.5°C/min in flowing air or nitrogen.

Films - DMAc solutions (15% solids) of the polymers and copolymers were centrifuged, the decantate doctored onto plate glass and dried at room temperature to a tack-free form in a dust proof chamber. The films on glass were dried 1 h each at 100, 200 and 300°C. Mechanical tests were performed according to ASTM D882 on at least four specimens per test condition.

Moldings - Polymers in a powder or fiberous form were compression molded in a 1.25 in square stainless steel mold using a hydraulic press equipped with electrically heated platens. Polymers were molded at ~50°C above their T_g s at pressures ranging from 100-500 psi. Four compact tension specimens (~0.62 x 0.62 x 0.30 in) were cut from the molding and tested according to a known procedure to determine fracture toughness.¹²

Results and Discussion

ATPAEs with calculated \bar{M}_n s of 3250 and 6500 g/mole were prepared by offsetting monomer stoichiometry. These oligomers had η_{inh} s of 0.12 and 0.18 dL/g and T_g s of 130 and 150°C, respectively, as shown in Table 1. When the oligomers were reacted with a stoichiometric amount of BTDA, the η_{inh} s increased to 0.54 and 0.63 dL/g and the T_g s increased to 179 and 177°C as expected. The high η_{inh} s obtained indicated that the calculated \bar{M}_n s were essentially correct.

The homopolymers and copolymers were characterized as shown in Table 2. The PI had an η_{inh} of 0.66 dL/g and a T_g at 295°C while the PAE η_{inh} was 0.35 dL/g and the T_g was 168°C, 127°C lower than the PI. A 1:1 blend of the polyamide acid and PAE homopolymers prepared by mixing DMAc solutions of each phase separated in solution. This blend also phase separated when the thoroughly mixed solution was dried at 300°C to form a film, whereby the polyamide acid was cyclized to the polyimide. A DSC sample containing both phases displayed the two T_g s of the homopolymers. However, a solution of the polyimide and the PAE in DMAc remained homogeneous for long periods without phase separating, but phase separation did occur when the solvent was removed to form a film.

Four different block copolymers were prepared as shown in Table 2 from the PAE and PI oligomers. The copolymers were prepared by reacting a stoichiometric

ratio of oligomers (using calculated \bar{M}_n s) producing polyamide acids with η_{inh} s ranging from 0.40 to 0.86 dL/g in DMAc (except as noted in Table 2). The cured polyimide films were characterized by DSC and results are also shown in Table 2. T_g s ranged from 203 to 248°C with the ATPAE 6500/ITPI 6500 block copolymer displaying two T_g s, at 203 and 252°C. The other block copolymers display T_g s which are essentially a rule of mixtures of the homopolymer T_g s.

The polymers and copolymers were subjected to thermogravimetric analysis in both flowing air and nitrogen at a heating rate of 2.5°C/min with results shown in Table 2 as temperature at 5% weight loss. The homopolymers displayed the highest thermal stability with decomposition temperatures approaching 500°C. The copolymers display slightly lower decomposition temperatures but are still very good for use temperatures below 200°C.

The homopolymers and block copolymers with equal length blocks were molded and machined into compact tension specimens. The PAE was molded at 200°C and 100 psi while the others were molded at ~350°C and 100 to 500 psi. The PAE has a fracture energy, G_{Ic} , twice as high as either the PI or the two block copolymers tested. It is discouraging that values lower than a rule of mixtures would predict were found.

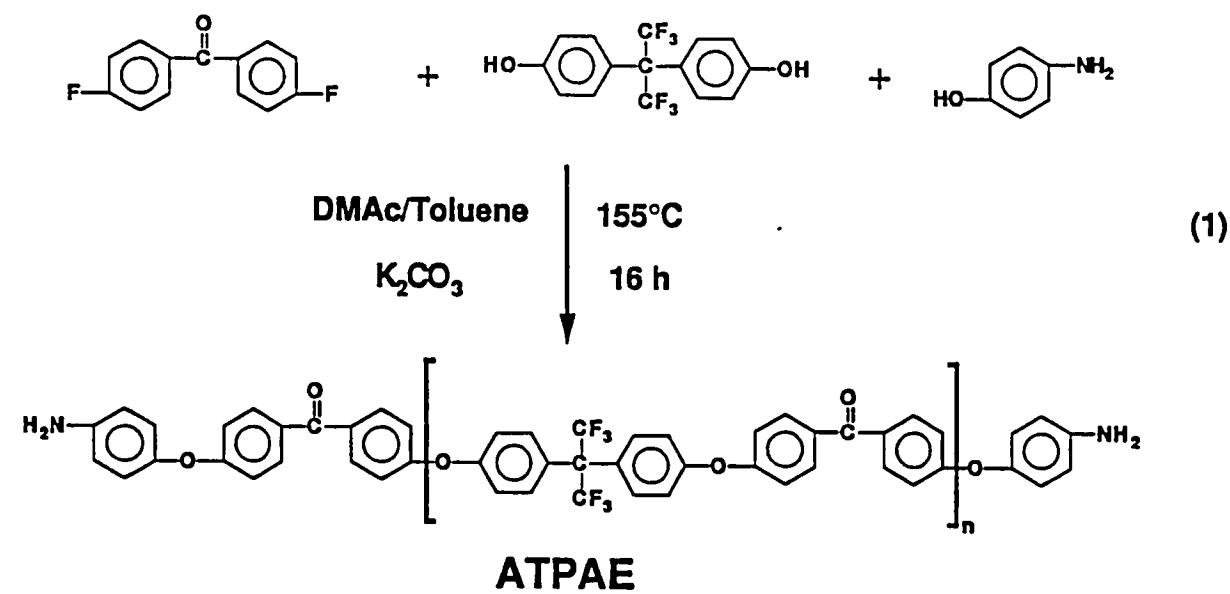
Tensile properties of the clear yellow-orange films of the copolymers and homopolymers are shown in Table 3. The polyimide has higher strength and modulus than the arylene ether as expected. The tensile strength and modulus of the copolymers varied widely but fall in between those of the homopolymers. For the copolymers, the PI(3250)/PAE(6500) displayed the lowest strength and modulus, as expected, and the PI(6500)/PAE(3250) displayed the highest strength but not the highest modulus.

Conclusions

A series of imide/arylene ether block copolymers were prepared using an arylene ether block containing a hexafluoroisopropylidene group and an imide block containing a hexafluoroisopropylidene and a trifluoromethyl group in the polymer backbone. The copolymers were characterized and mechanical properties were determined and compared to the homopolymers. Future work will study the stability of these polymers to electron radiation.

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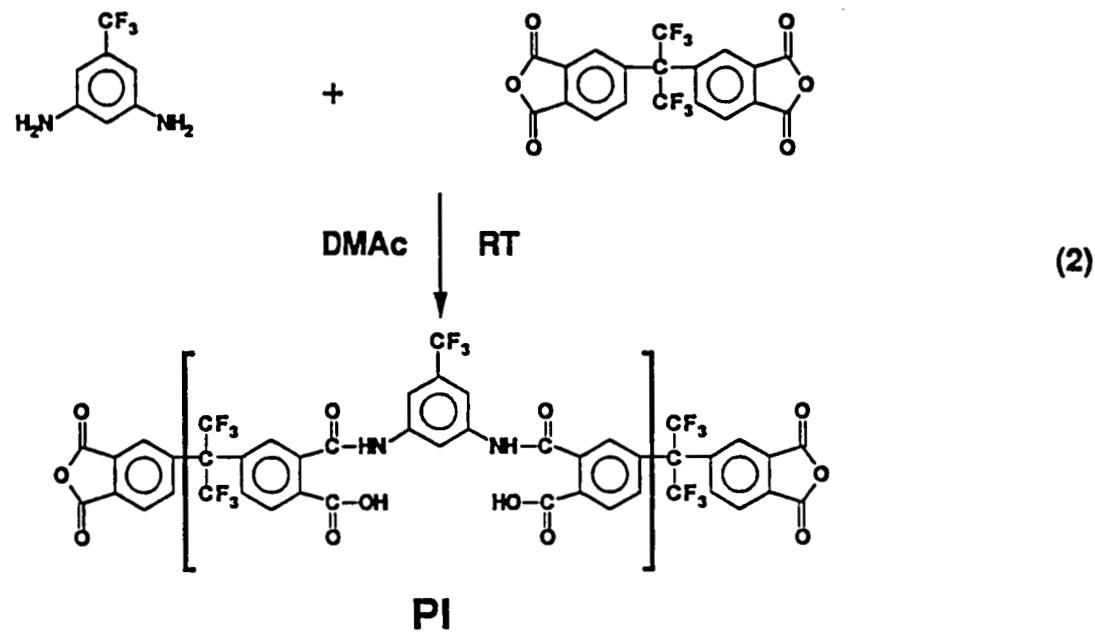


TABLE 1. CHARACTERIZATION OF OLIGOMERS AND POLYMERS

Oligomer or Polymer	η_{inh} , dL/g	T _g , °C by DSC
ATPAE 3250	0.12	130
ATPAE 6500	0.18	150
ATPAE 3250/BTDA	0.54	179
ATPAE 6500/BTDA	0.63	177

TABLE 2. CHARACTERIZATION OF POLYMERS AND BLOCK COPOLYMERS

Copolymer	η_{inh} , dL/g (Polyamide acid)	T_g , °C by DSC	T_{dec} , °C		G_{Ic} , in-lbs/in ²
			N_2	Air	
PI(3250)/PAE(3250)	0.70	225	420	419	8.5
PI(6500)/PAE(3250)	0.86	248	419	434	---
PI(3250)/PAE(6500)	0.49 ^a	203	458	444	---
PI(6500)/PAE(6500)	0.40	203,252	486	461	8.5
PI	0.66	295	496	486	8.6
PAE	0.35	168	493	476	16.8

^aMeasured on solution imidized polyimide.

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TABLE 3. MECHANICAL PROPERTIES OF POLYMERS AND
BLOCK COPOLYMER FILMS AT 25°C

Polymer or Block Copolymer	Tensile Yield, ksi	Tensile Strength at Break, ksi	Tensile Modulus, ksi	Elongation at Break, %
PI(3250)/PAE(3250)	13.5	13.1	386	7.4
PI(6500)/PAE(3250)	15.0	15.0	400	6.2
PI(3250)/PAE(6500)	11.6	11.7	354	5.8
PI(6500)/PAE(6500)	13.8	13.8	424	4.7
PI	16.9	16.9	443	5.9
PAE	9.5	8.9	325	9.9

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